



Preparation of basic lead oxide from spent lead acid battery paste via chemical conversion

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ABSTRACT

A process with potentially reduced environmental impact was studied to recover lead as ultra-fine lead oxide from lead paste in spent lead acid batteries. The lead paste was desulfurized first and then reacted with citric acid to produce lead citrate. Finally, lead citrate was calcined at low-temperature to obtain ultra-fine lead oxide. The desulfurized paste, lead citrate and the recovered lead oxide were characterized by XRD. When desulfurized by Na_2CO_3 , NaHCO_3 or $(\text{NH}_4)_2\text{CO}_3$, the desulfurization rate of lead paste was over 99.0% under initial C/S ratio of 2, 35 °C, and slurry density of 100 g/L. The lead carbonate and basic lead carbonate could be prepared from desulfurized paste, which was acidified with CO_2 gas after being desulfurized by sodium carbonate. The lead citrate precursor, $\text{Pb}(\text{C}_6\text{H}_5\text{O}_7) \cdot \text{H}_2\text{O}$, was prepared by leaching desulfurized paste with citric acid and H_2O_2 . Ultra-fine PbO/Pb powder with particle size of 100–500 nm was obtained at 370 °C. This process is found to be simple, pollution-free and high efficient in the recovery of valuable lead oxide from spent lead acid battery paste, which can replace the traditional smelting method.

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1. Introduction

Lead acid batteries (LABs) are low-cost in manufacturing, simple to design, reliable and safe, compared with nickel–cadmium (NiCd) batteries, lithium ion batteries (LIBs) and other electrochemical batteries. Given these advantages, the need for LABs as a power source in starting, lighting and ignition of engine (SLI) for vehicular (e.g., automotive, marine and aviation) is tremendous and has been steadily increasing in recent years since electric bicycles and electric cars have come to claim the market (Chen et al., 2009). Predictably, the production of lead batteries will continue to rise even more sharply when the high-capacity lead acid batteries are included in industrial application. In 2010, the consumption of refined lead was 4.21 million tons, 80% of which was used for lead–acid batteries in China. Massive production also generates massive pollution from spent and discarded batteries. It is estimated that the amount of waste lead batteries would be multiplied annually based on the mean lifetime of 2–3 years (Barkleit et al., 1999; Zhou, 2007). It is also reported that, in China alone, more than 95% of spent and discarded lead batteries are collected and recycled to reclaim the lead for further lead battery production.

Spent LABs consist of four parts, which are 11–30 wt.% electrolyte, 24–30 wt.% lead and lead alloy grid, 30–40 wt.% lead paste, and 22–30 wt.% organics and plastics. Among them, spent lead paste is complex, mainly comprising PbSO_4 (~60%), PbO_2 (~28%) and PbO (~9%), and a small amount of lead metal (~3%). This complexity leads to many difficulties in the subsequent processing (Chen and Dutrizac, 1996; Ferracin et al., 2002). Commonly, lead paste is recovered as lead through an energy-intensive decomposition process, i.e. traditional pyrometallurgical process. Decomposition of PbSO_4 requires relatively high temperature (> 1000 °C), using coal or coke as the source of energy with emissions of both SO_2 gas and lead particulate in the pyrometallurgical process. Thus, more and more attention is paid to the green recycling process for spent lead acid battery, such as those involving hydrometallurgical routes (Rabah and Barakat, 2001; Vaysgant et al., 1995).

The hydrometallurgical recovery process of the treatment of lead paste without electrowinning is not really performed so far. This leads to the need to develop an effective, low cost and environment-friendly recycling process for spent lead battery paste. A novel patented technology of recovering lead has been developed by Kumar et al. (2006). In this process, spent lead acid battery paste was treated with aqueous citric acid solution to generate a lead citrate precursor which was separated from soluble sulfate solution (Sonmez and Kumar, 2009a,b). Lead could be recovered as ultra-fine lead oxide powder after calcination of lead citrate precursors (Zhu et al., 2010). However, the reaction rate of this leaching process is slow, and the separation and recovery of filtrate (including Na_2SO_4 , $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ and $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$) is difficult.

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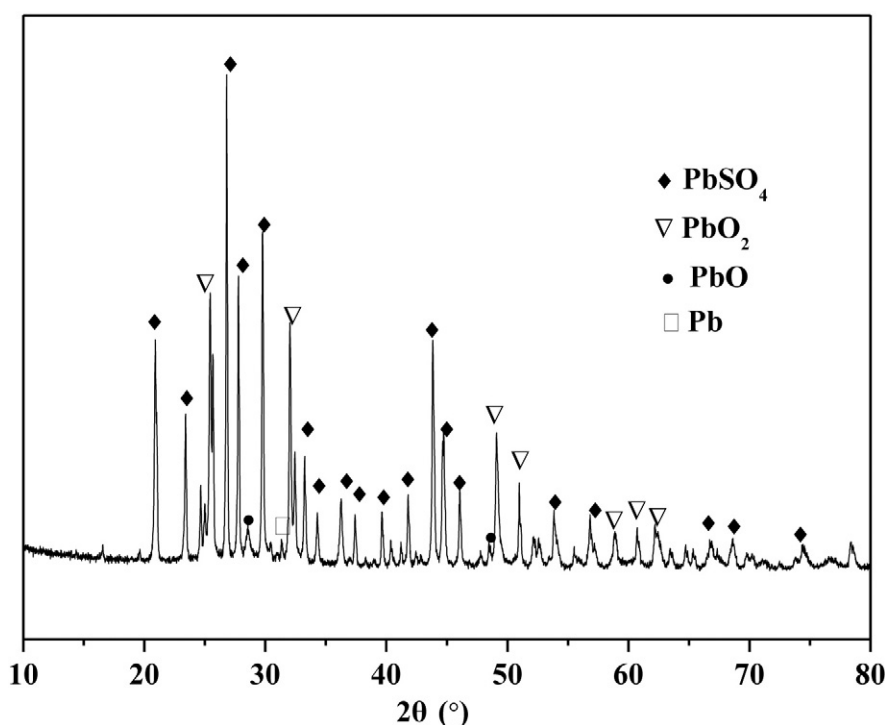


Fig. 1. XRD pattern of the fine lead paste.

The objectives of this work are to seek for a valid and efficient alternative for lead recovery from lead paste in solution through chemical conversion. Firstly, lead paste can be converted into desulfurized paste with desulfurizing agent. Secondly, desulfurized paste is leached with citric acid solution to generate lead citrate precursor of $\text{Pb}(\text{C}_6\text{H}_5\text{O}_7) \cdot \text{H}_2\text{O}$. Thirdly, ultra-fine lead oxide is prepared by combustion–calcination of lead citrate precursor at low temperature. The new process comprising desulfurization, leaching and combustion–calcinations has been carried out in laboratory scale.

2. Experimental

2.1. Chemicals and materials

Lead paste used in the work was provided by Hubei Jinyang metallurgical Co., LTD, a company specializing in the recovery of spent and discarded LABs. The dried reddish powder sample of lead paste was separated by sieving process. And then the battery grid plate (oversize) was separated from fine lead paste (undersize). In this work, fine lead paste less than 120 mesh size was only used in the leaching tests in order to eliminate the negative effect of nonhomogeneity of particle size. The XRD pattern of the fine lead paste is shown in Fig. 1. The sample contained a large amount of PbSO_4 , and PbO_2 , together with minor quantity of PbO and metallic Pb . Chemical compositions of paste sample were analyzed by the chemical titration method, listed in Table 1. The content of total lead in the fine lead paste specimen is 74.5%.

2.2. Desulfurization and leaching procedure

The flowsheet of the process designed in this work is shown in Fig. 2. A size-separation pretreatment was carried out to separate grid plate particles and other impurities from lead paste. The separated fine lead paste (undersize) was then used in the following desulfurization process. The desulfurization was performed in a beaker immersed in a thermostatic water bath at $35 \pm 2^\circ\text{C}$ under mechanic agitation to keep solid particle suspension during conversion

experiments. 100 g of the separated fine lead paste was added to 1000 mL desulfurization solutions of specified concentration. Three typical reagents for the desulfurization were investigated, i.e. Na_2CO_3 , NaHCO_3 , and $(\text{NH}_4)_2\text{CO}_3$. The different mole ratios of CO_3^{2-} to SO_4^{2-} or HCO_3^- to SO_4^{2-} , called as C/S, were investigated, i.e. 1.0, 1.5, 2.0, and 2.5 with solid content of 100 g/L. After completion of the desulfurization reaction, the collected solids were washed with distilled water, then filtered and dried at 60°C to obtain desulfurized paste. The amount of unconverted S in the desulfurized paste was analyzed by the High-frequency Infrared Carbon & Sulfur Analyzer (HCS-140, Shanghai DeKai Instrument Co., Ltd. China). The desulfurization rate of lead paste was calculated through the following Eq. (1).

$$\text{Desulfurization rate} = [(W_1 \times C_1 - W_2 \times C_2) / (W_1 \times C_1)] \times 100\%. \quad (1)$$

Where W_1 is the mass of spent lead acid battery paste, C_1 is the mass percentage of S of spent lead acid battery paste, W_2 is the mass of desulfurized paste sample, and C_2 is the mass percentage of S of desulfurized paste sample. Sulfate ion in the filtrate was quantitatively determined by the gravimetric method (EPA Method 375.3., 1978). The data was used to check the results of the analysis of S in solid phase in order to deduce sulfur balance.

The leaching process was also carried out in a thermostatic water bath. 100 g of desulfurized paste was added into 500 mL of citric acid solution and then leaching was carried out at ambient temperature ($25 \pm 2^\circ\text{C}$). Hydrogen peroxide (60 mL) was added as the reduction

Table 1

Chemical compositions of lead paste sample from spent LABs (wt.%).

Composition	Sludge composition (wt.%)
PbSO_4	64.5
PbO_2	29.5
PbO	4.5
Pb	0.5
Total lead	74.5

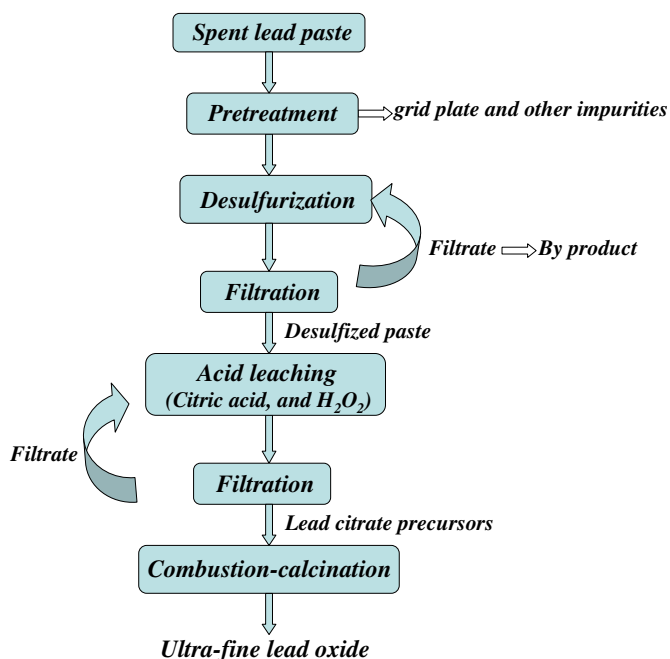
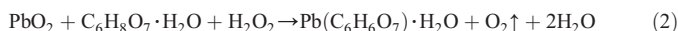


Fig. 2. Flowsheet of the recycling process for lead paste in spent LABs.

agent to convert lead (IV) into lead (II) (Sonmez and Kumar, 2009a). The chemical reaction is shown in Eq. (2).



After the leaching, the precipitated product of lead citrate precursor was filtered. Then the solid phase was washed with distilled water and dried at 65 °C. The concentration of lead ion in the filtrate solution was analyzed by AAS (WFX-120).

2.3. Combustion-synthesis product from lead citrate precursor

The lead citrate precursor was calcined at 370 °C for 1 h in static air. The weight loss was checked by weighing for each set of the experiments. The crystalline phases and morphologies of the combustion-synthesis products were investigated by a powder X-ray diffraction (XRD) and Scanning electron microscopy (SEM), respectively.

2.4. Material/product characterization

XRD pattern data of powder samples were collected using a X-ray diffractometer X'Pert PRO XRD (Philips, PANalytical B.V., Holland) with Cu K α radiation and $\lambda = 1.54 \text{ \AA}$. Thermal analyses of lead citrate precursor was performed in alumina crucibles by Diamond TG/DTA (PerkinElmer Instruments) under air flow of $20 \text{ cm}^3 \cdot \text{min}^{-1}$ at the heating rate of $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ from room temperature to 600 °C. Morphological studies of the lead citrate precursor and the combustion-synthesis product were carried out with SEM (Sirion 200, FEI, Holland), which was operated at 10 kV after coating the samples with gold.

3. Results and discussion

3.1. Desulfurization of lead paste

Fig. 3 presents the effect of different C/S on desulfurization rate of lead paste. Desulfurization rate slightly increased with the increase in the C/S mole ratio, and reached over 98% at the C/S mole ratio of 2.0. When the C/S mole ratio was more than 2.0, desulfurization rate was

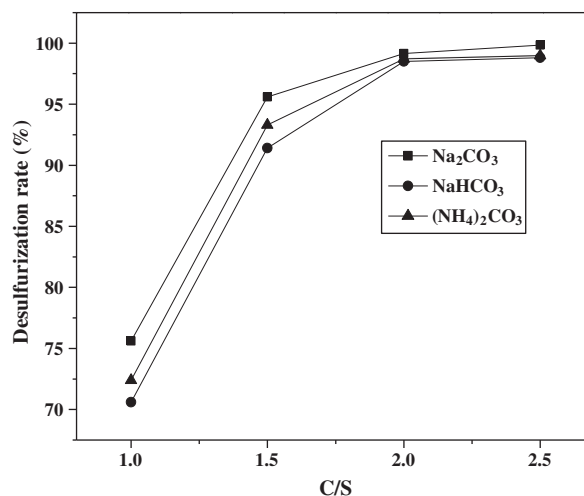


Fig. 3. Effect of C/S mole ratio on the desulfurization rate (reaction temperature of 35 °C, solid content of 100 g/L, reaction time of 60 min).

kept approximately constant. Compared with sodium bicarbonate and ammonium carbonate, sodium carbonate was more efficient for the desulfurization of lead sulfate.

Arai and Toguri (1984) had investigated the leaching reactions of pure lead sulfate in sodium carbonate solutions. Based on experimental results of both thermodynamics and kinetics, a mass transfer model based on the diffusion of CO_3^{2-} through a solution boundary layer was established to account for the leaching rates. Gong et al. (1992a) researched the reaction of different size of PbSO_4 powder with Na_2CO_3 media under a broad range of experimental conditions. The experimental results supported a mechanism of mass transport control by carbonate ions through the constantly thickening product layer formed on the agglomerated PbSO_4 particles.

Fig. 4 shows the effect of desulfurization time on desulfurization rate of lead paste. The desulfurization rate of about 98.0% was obtained in 60 min at 35 °C when sodium carbonate, sodium bicarbonate or ammonium carbonate was used as the desulfurization reagent. In the desulfurization of lead sulfate, the difference in the carbonation power between sodium bicarbonate and ammonium carbonate was not

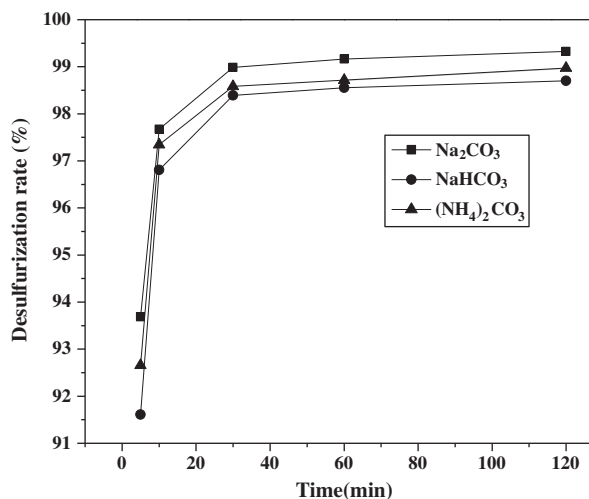


Fig. 4. Effect of reaction time on desulfurization rate (reaction temperature of 35 °C, solid content of 100 g/L, C/S of 2).

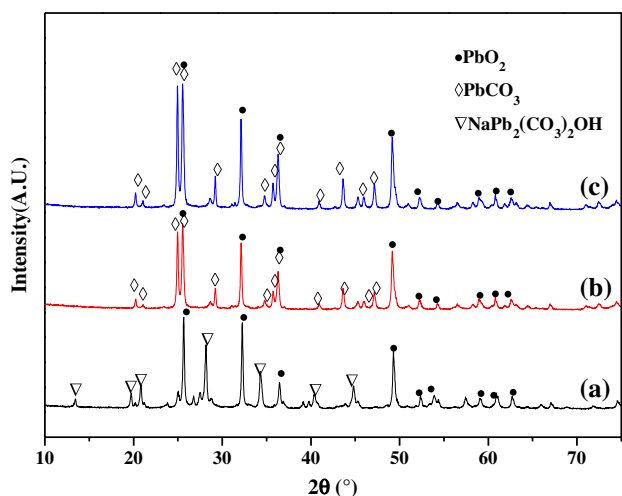


Fig. 5. XRD pattern of desulfurized paste with different desulfurizing reagents: (a) Na_2CO_3 , (b) NaHCO_3 , and (c) $(\text{NH}_4)_2\text{CO}_3$.

obvious. The sulfate ion concentration of the paste was only 0.05% after 60 min desulfurization treatment, which could be satisfactory in the following hydrometallurgical process of desulfurization.

The XRD patterns of different desulfurized paste are shown in Fig. 5. In the XRD patterns of all desulfurized paste, peaks of lead sulfate disappeared, and lead (IV) dioxide became the main crystalline product, which indicated the high desulfurization efficiency. The lead carbonate was identified in the desulfurized paste from the desulfurization reaction with sodium bicarbonate or ammonium carbonate, while $\text{NaPb}_2(\text{CO}_3)_2\text{OH}$ was identified as desulfurization conversion product in the paste with the desulfurization reagent of sodium carbonate, as shown in Fig. 5.

The different chemical desulfurization reactions are given by the following Eqs. (3)–(7).



There were convincing proofs that these reactions not only increased the reagent consumption but also resulted in difficulties in the subsequent processing and the use of the final products. These compounds contained Na^+ in form of $\text{NaPb}_2(\text{CO}_3)_2\text{OH}$, depending on the pH values of the solution (Arai and Toguri, 1984; Gong et al., 1992b).

In order to avoid introducing impurity of the sodium compound, $\text{NaPb}_2(\text{CO}_3)_2\text{OH}$ prepared by desulfurization of paste with sodium carbonate could be acidified with CO_2 gas to adjust pH.

The chemical reaction in the solution with carbon dioxide is given by the following Eq. (8).



When the solid content of 100 g/L, the intermediate products (including $\text{NaPb}_2(\text{CO}_3)_2\text{OH}$) desulfurization were acidified with CO_2 for 5 min at a temperature of 25 °C. The main products (including PbCO_3 and $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$) were separated from the solution, which was identified with XRD technique as shown in Fig. 6.

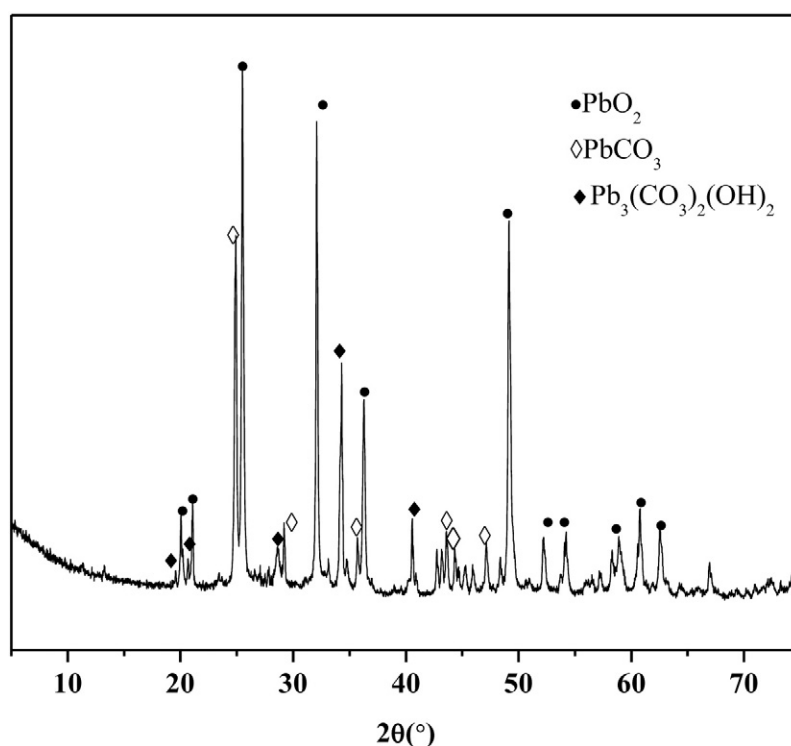


Fig. 6. XRD pattern of the acidified product.

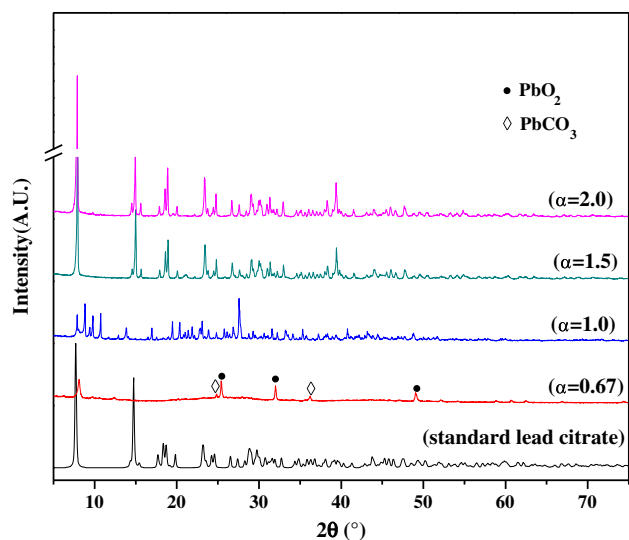
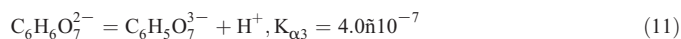
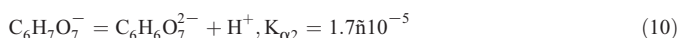
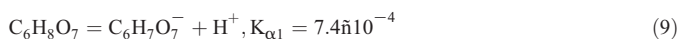


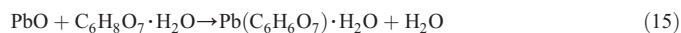
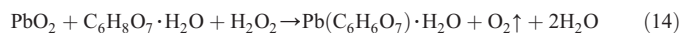
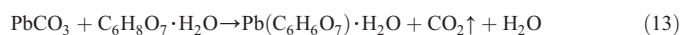
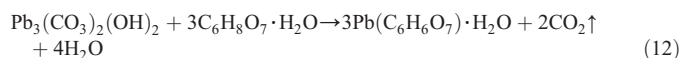
Fig. 7. XRD pattern of lead citrate precursor prepared with different α (reaction temperature of 25 °C, solid density of 200 g/L, reaction time of 1 h).

3.2. Leaching with citric acid

Citric acid is a common weak organic acid. One $C_6H_8O_7$ molecule contains three carboxyls and 3 mol H^+ should be theoretically produced, upon dissociation of 1 mol citric acid in distilled water. But, in fact, H^+ of the acid can not be completely ionized. The dissociation reaction of citric acid can be expressed as the following Eqs. (9)–(11).



The major components of desulfurized paste were $Pb_3(CO_3)_2(OH)_2$, $PbCO_3$, PbO_2 and PbO . The reactions between desulfurized paste and citric acid in the pH of 3–4 may be given as the following Eqs. (12)–(15).



The following leaching tests were carried out at 25 °C, and the solid content was 200 g/L.

The XRD patterns of crystallized products prepared with different reagent dosages are shown in Fig. 7. When the mole ratio of $C_6H_8O_7 \cdot H_2O$ to Pb (α) was 0.67, $PbCO_3$ and PbO_2 were identified. The results indicated that conversion of $PbCO_3$ and PbO_2 was not complete. With the increasing of α , the XRD pattern of the precursor matched better with standard structural data of lead citrate. These patterns matched well with standard XRD patterns database of lead citrate ($PbC_6H_6O_7 \cdot H_2O$) (Kourgiantakis et al., 2000) when the value of α was above 1.5. However, there was a special peak at 2θ of around 39°, which was significantly different from peaks of standard database of lead citrate. This result may possibly lie in the fact that the lead citrate precursor is a kind of lead organic compound, such as lead–citrate complex with varying co-ordination number of citrate and crystal water. Single-crystal X-ray diffraction data will be collected

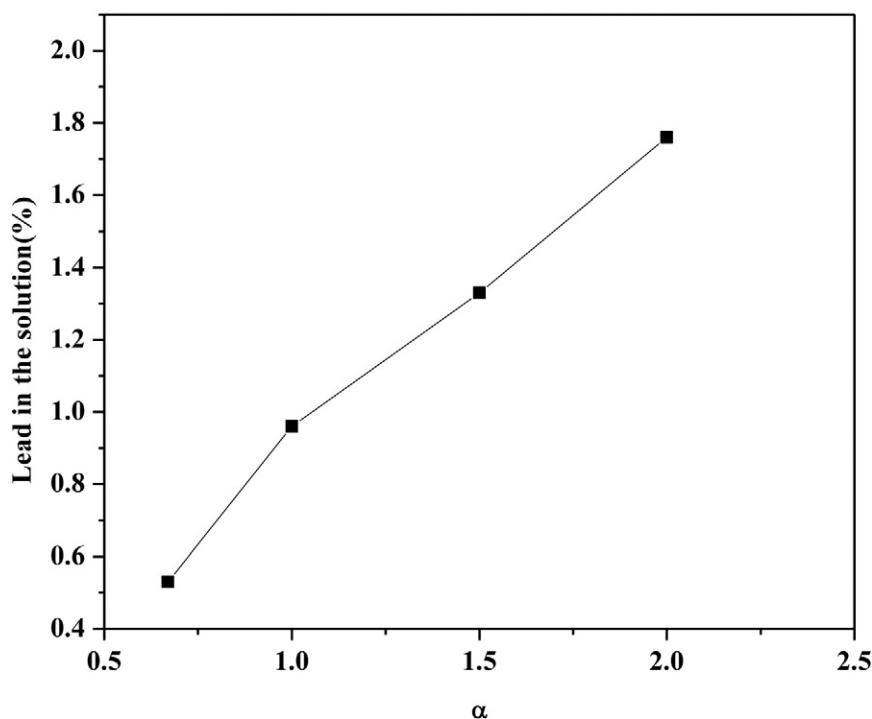


Fig. 8. The amount of lead kept in the filtrate with different α (reaction temperature of 25 °C, solid density of 200 g/L, reaction time of 1 h).

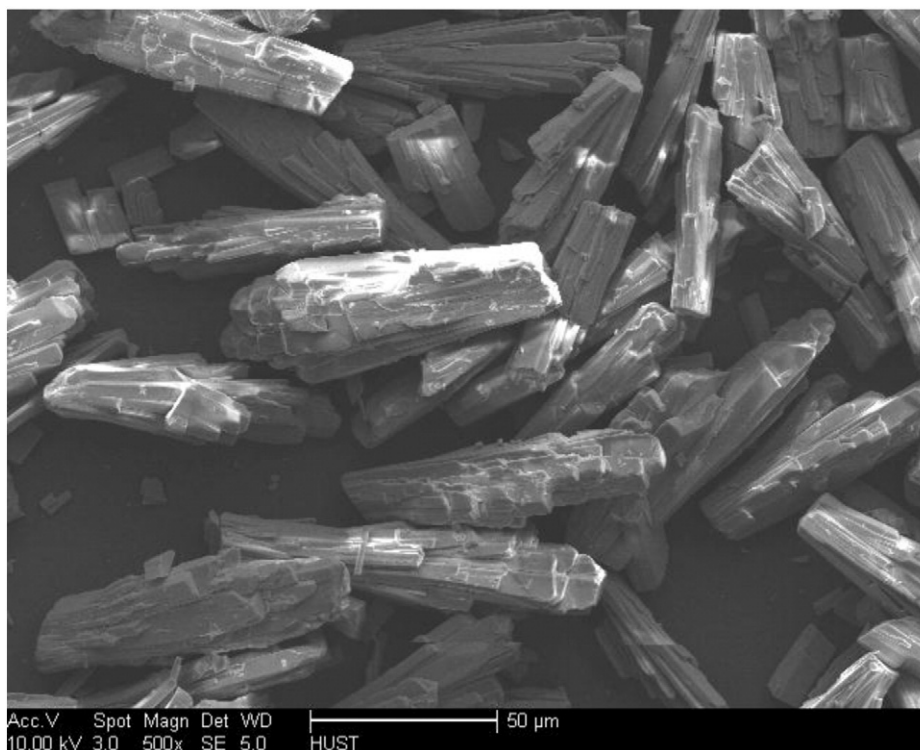


Fig. 9. SEM image of the lead citrate precursor (α of 2, reaction temperature of 25 °C, solid density of 200 g/L, reaction time of 1 h).

in order to provide detailed information about crystal structure of the lead citrate precursor in further study.

Some lead probably remained in the filtrate since lead citrate had certain solubility in citric acid solution. Thus, it is important to minimize the amount of lead in the filtrate to gain a higher recovery of lead. Fig. 8 showed the amount of soluble lead in the filtrate with different α under the same leaching conditions: 100 g/L, 25 °C, and 1 h. With an increase of α , lead concentration in the filtrate increased significantly due to the larger excess of citric acid in leaching solution. The residual lead in the solution was 3.0% remaining in solution when α was 1.5, which could be considered as the optimal condition for the leaching.

The morphology of $\text{Pb}(\text{C}_6\text{H}_5\text{O}_7) \cdot \text{H}_2\text{O}$ from the leaching of desulfurized paste was investigated by SEM analysis (Fig. 9). The $\text{Pb}(\text{C}_6\text{H}_5\text{O}_7) \cdot \text{H}_2\text{O}$

sample had a similar morphology with both PbO and PbO_2 (Sonmez and Kumar, 2009a).

3.3. The thermal decomposition of lead citrate

The thermal decomposition of the lead citrate precursor from room temperature to 600 °C in air atmosphere is shown in Fig. 10. According to the TG results, the first stage of weight loss of the precursors in air was observed in the range of 20–180 °C, and the obvious endothermic peaks at 170 °C could be regarded as the dehydration of lead citrate. The second stage of weight loss of the precursor in air was observed in the range of 180–410 °C. The total loss of mass accompanying the thermal reactions of precipitates was about 48.5%, which is consistent with weight loss of stoichiometric thermal decomposition of $\text{Pb}(\text{C}_6\text{H}_5\text{O}_7) \cdot \text{H}_2\text{O}$. When the temperature was higher than 400 °C, both weight loss and heat flow were stable. The results suggested that the decomposition of lead citrate precursor was complete at and above 400 °C. Therefore, the calcination temperature of the lead citrate precursor for preparation of PbO could be lower than 400 °C.

The prepared lead oxide powder was characterized by XRD and SEM. Fig. 11 showed the XRD pattern of the products calcined in air at 370 °C for 1 h. The products were mainly massicot (orthorhombic lead oxide) and lead metal. Fig. 12 showed the SEM image of the products via combustion in air atmosphere for 1 h. As shown in Fig. 12, the particle size of the product was in range of 100 to 500 nm.

4. Conclusions

In this study, an innovative, environmentally less harmful route was proposed to replace the traditional smelter recycling process of spent lead acid battery paste. Desulfurization of spent lead paste and the thermal decomposition of lead citrate precursor have been carried out in laboratory scale. The effects of C/S mole ratios on the desulfurization efficiency were investigated. The conversion of desulfurization reached the equilibration basically when the C/S mole ratio was above 2. Lead carbonate and basic lead carbonate were identified

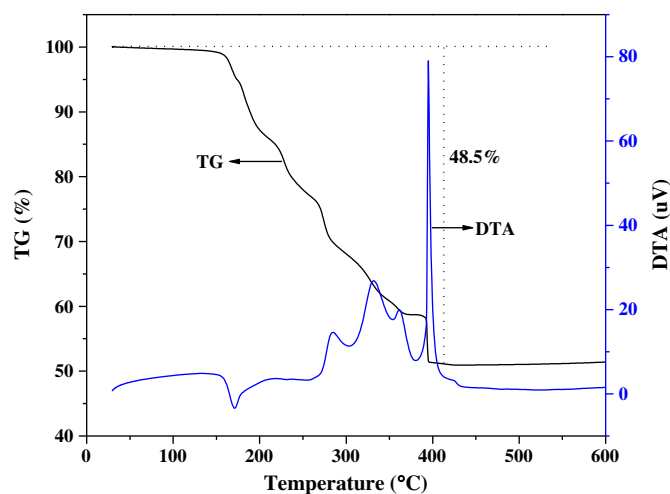


Fig. 10. TG-DTA curve of the lead citrate precursor (α of 2, reaction temperature of 25 °C, solid density of 200 g/L, reaction time of 1 h).

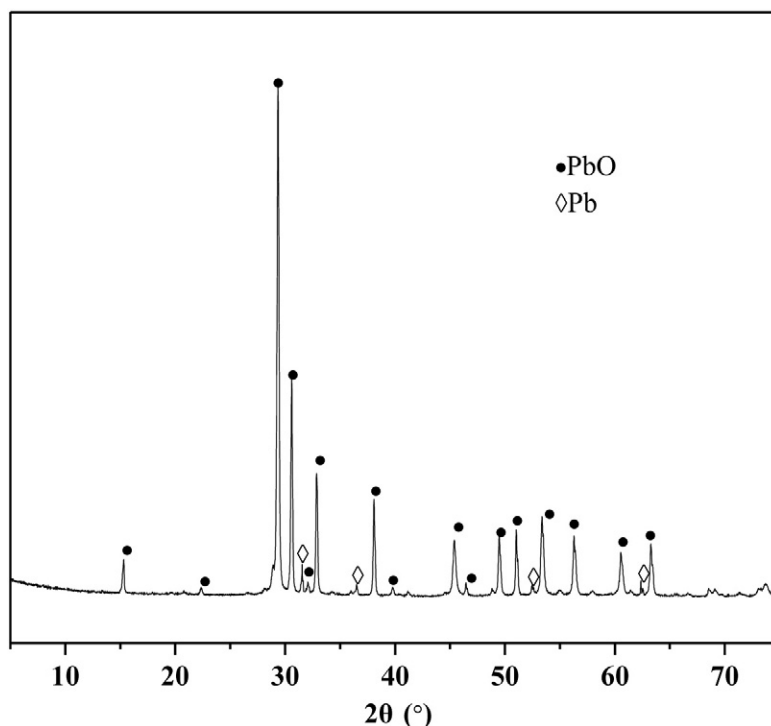


Fig. 11. XRD pattern of combustion-calcination products at 370 °C for 1 h.

as desulfurization product. In the leaching process of desulfurized paste with citric acid, leaching efficiency of lead was found to be increased with an increase in the concentration of the citric acid, while the recovery efficiency of lead was decreased. Lead citrate ($\text{Pb}(\text{C}_6\text{H}_6\text{O}_7) \cdot \text{H}_2\text{O}$) was the only leaching product when the mole ratio of $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ to Pb (α) was above 1.5. The ultra-fine lead oxide powder composed

mainly of β -PbO, with particle size of 100–500 nm, was successfully obtained by calcining at a temperature of 370 °C for 1 h. Several advantages were observed when compared with the traditional processes, such as the elimination of SO_2 gas emission and lead particulates, lower energy consumption, recovered products of ultra-fine lead oxide with higher surface areas. The preliminary studies in the current

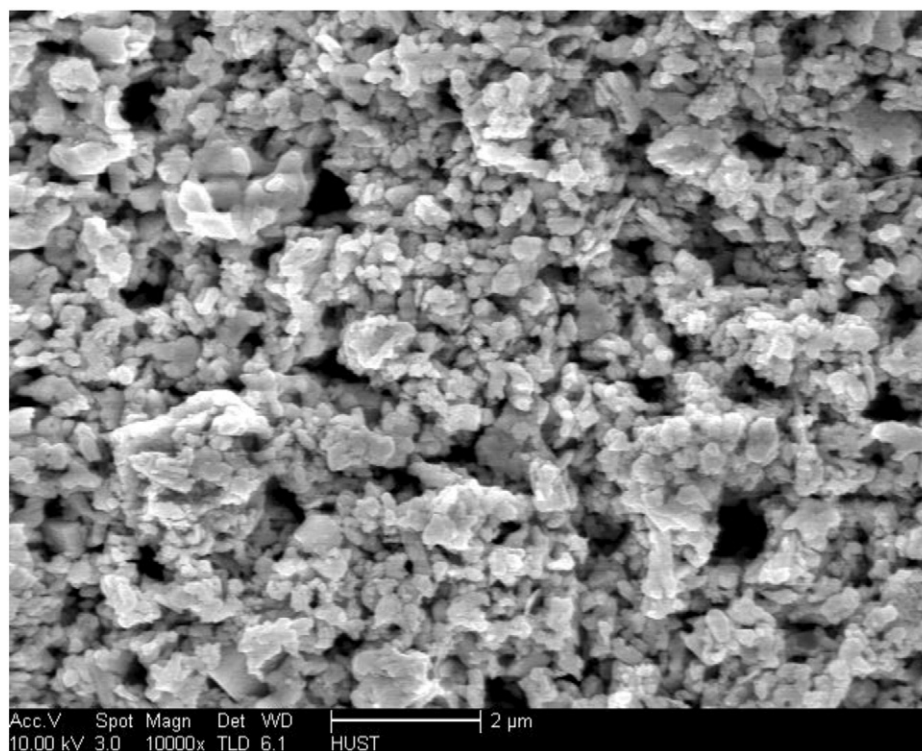


Fig. 12. SEM image of combustion-calcination products at 370 °C for 1 h.

report showed that this process could be efficient to recover and recycle lead paste as lead oxide from spent lead paste.

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References

- Arai, K., Toguri, J.M., 1984. Leaching of lead sulphate in sodium carbonate solution. *Hydrometallurgy* 12, 49–59.
- Barkleit, G., et al., 1999. Electrodeposited, dispersion-hardened, lightweight grids for lead–acid batteries. *J. Power. Sources* 78 (1–2), 73–78.
- Chen, T.T., Dutrizac, J.E., 1996. The mineralogical characterization of lead acid battery paste. *Hydrometallurgy* 40, 223–245.
- Chen, H.Y., Li, A.J., Finlow, D.E., 2009. The lead and lead–acid battery industries during 2002 and 2007 in China. *J. Power. Sources* 191 (1), 22–27.
- Ferracin, L.C., et al., 2002. Lead recovery from a typical Brazilian sludge of exhausted lead–acid batteries using an electrohydrometallurgical process. *Hydrometallurgy* 65 (2–3), 137–144.
- Gong, Y., Dutrizac, J.E., Chen, T.T., 1992a. The conversion of lead sulphate to lead carbonate in sodium carbonate media. *Hydrometallurgy* 28, 399–421.
- Gong, Y., Dutrizac, J.E., Chen, T.T., 1992b. The reaction of anglesite (PbSO_4) with sodium carbonate solutions. *Hydrometallurgy* 31, 175–199.
- Kourgiantakis, M., et al., 2000. Lead–citrate chemistry synthesis, spectroscopic and structural studies of a novel lead (II)–citrate aqueous complex. *Inorg. Chim. Acta* 297, 134–138.
- Kumar, R.V., Sonmez, M. S. and Kotzeva, V. P. UK Patent Application No: 0622249.1, 2006; Patent PCT/GB2007/004222; WO2008/056125.
- Rabah, M.A., Barakat, M.A., 2001. Energy saving and pollution control for short rotary furnace in secondary lead smelters. *Renew. Energy* 23 (3–4), 561–577.
- Sonmez, M.S., Kumar, R.V., 2009a. Leaching of waste battery paste components. Part 1: lead citrate synthesis from PbO and PbO_2 . *Hydrometallurgy* 95 (1–2), 53–60.
- Sonmez, M.S., Kumar, R.V., 2009b. Leaching of waste battery paste components. Part 2: leaching and desulphurisation of PbSO_4 by citric acid and sodium citrate solution. *Hydrometallurgy* 95 (1–2), 82–86.
- Sulfate by Gravimetric Determination, EPA Method 375.3. <http://www.caslab.com/EPA-Method-375.3/.pdf>1978.
- Vaysgant, Z., et al., 1995. A low-temperature technique for recycling lead/acid battery scrap without wastes and with improved environmental control. *J. Power. Sources* 53, 303–306.
- Zhou, H.W., 2007. Characters of the waste lead acid storage battery and its melting technology options. *Resour. Recycl.* 5, 9–22 (in Chinese).
- Zhu, X.F., et al., 2010. Preparation of ultra-fine PbO powders from lead paste in spent lead acid battery. *Chin. J. Nonferrous Met.* 20 (1), 132–136 (in Chinese).